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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>3</sup> : C07D 251/16, 251/22, 405/04, 403/04	A1	(11) International Publication Number: WO 81/03020 (43) International Publication Date: 29 October 1981 (29.10.81)
(21) International Application Number: PCT/AU81/00046 (22) International Filing Date: 22 April 1981 (22.04.81) (31) Priority Application Number: PE 3241/80 (32) Priority Date: 22 April 1980 (22.04.80) (33) Priority Country: AU (71) Applicant (for all designated States except US): COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION [AU/AU]; Limestone Avenue, Campbell, A.C.T. 2601 (AU). (72) Inventor; and (75) Inventor/Applicant (for US only): HARRIS, Roger, Lawrence, Newton [AU/AU]; 8 Wolgal Place, Aranda, A.C.T. 2614 (AU). (74) Agents: SLATTERY, John, M. et al.; Davies & Collison, 1 Little Collins Street, Melbourne, Vic. 3000 (AU).		(81) Designated States: AU, CH (European patent), DE (European patent), FR (European patent), GB (European patent), JP, US. Published With international search report With amended claims and statement
(54) Title: TRIAZINE SYNTHESIS (57) Abstract <p>A process for the synthesis of substituted 1, 3, 5-triazine compounds of the general formula:</p> <div style="text-align: center;"> </div> <p>wherein R<sup>1</sup> and R<sup>2</sup>, which may be the same or different, are selected from the group consisting of hydrogen, halogen, alkoxycarbonyl, alkyl, substituted alkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkylamino, dialkylamino, arylamino, alkyl-aryl amino, alkylthio, arylthio, alkoxy and aryloxy (provided that R<sup>1</sup> and R<sup>2</sup> are not both halogen); and R<sup>3</sup> is selected from the group consisting of halogen, alkylamino, dialkylamino, arylamino, alkyl-aryl amino and N-heteroaryl; comprises reaction of a substituted halomethyleneiminium salt with a substituted N-cyanoamidine, N-cyanoguanidine, N-cyanocarbamidate or N-cyanocarbamidothioate. Substituted 1, 3, 5-triazine compounds having fungal germination inhibition properties are also disclosed. The following compounds 1) 2-chloro-4-phenyl-1, 3, 5-triazine, 2) 2-chloro-4-phenoxyethyl-6-phenyl-1, 3, 5-triazine, 3) 2-N-methylphenylamino-4-phenyl-1, 3, 5-triazine, 4) 2-chloro-4-cyanomethyl-6-phenyl-1, 3, 5-triazine are also disclosed and claimed.</p>		

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## TRIAZINE SYNTHESIS

This invention relates to a process for the synthesis of 1,3,5-triazine compounds, including in particular mono- or di-alkyl or -aryl substituted 1,3,5-triazines.

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1,3,5-Triazines are a class of heterocyclic compounds finding widespread use in many areas of chemical industry - notably as intermediates in plastics manufacture and as herbicides in agriculture. Other triazines are used in disinfectants, algaecides, pharmaceuticals and explosives.

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In practice, much of the industrial significance of triazines is confined to the symmetrical triazines including 2,4,6-trihydroxy-s-triazine (cyanuric acid), 2,4,6-triamino-s-triazine (melamine), and 2,4,6-trichloro-s-triazine (cyanuric chloride) and their derivatives, and the chemistry of these compounds has been widely studied; in part because of their ease of synthesis. Despite their intrinsic interest, however, mono- and di-alkyl or -aryl triazines have received relatively little attention. The primary reason for this appears to be the lack of availability of suitable general synthetic methods for this class of triazine derivatives. For example, of the twelve or so methods presently available for the synthesis of this class of triazines few are of preparative value for triazines bearing two alkyl or aryl groups.

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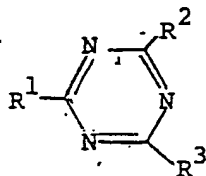
N-Cyanoamidines, potentially useful as starting materials for heterocyclic ring formation, have heretofore received scant attention, despite their ready availability from imidates or amidines (K.R.Huffman and F.C.Schaefer, J. Org. Chem., 28, 1812, (1963).), (J.T.Shaw and R.Adams, J. Chem. Eng. Data, 13, 142, (1968).) Their conversion to 1,3,5-triazines by condensation with amides, imidates, amidines and nitriles under a variety of conditions was described by Huffman and Schaefer (supra), but yields were disappointing (15-50%). More recently, low yields of iminodihydrotriazines have been reported (W.Ried and N. Kothe, Chem. Ber., 109, 2706, (1976)) in the reaction of N-cyanoamidines with N-substituted chloroformamidines and imidoyl chlorides, and in one case a 1,3,5-triazine isolated. Attention has now been given to the reaction of N-cyanoamidines, N-cyanoguanidines, N-cyanocarbamimidates or N-cyanocarbamidothioates with halomethyleneiminium salts, leading to the development of a novel synthesis of 1,3,5-triazines which is both versatile and convenient to carry out.

The novel synthesis of triazines from N-cyanoamidines, N-cyanoguanidines, N-cyanocarbamimidates or N-cyanocarbamidothioates and halomethyleneiminium salts in accordance with the present invention is of particular value since it can be successfully applied to the preparation of a wide range of triazine derivatives in which one or two of the substituents is an alkyl or an aryl substituent. Furthermore, by the appropriate choice of starting materials, triazines bearing a hydrogen substituent are also easily available.



The yields are generally high (up to 90%) and the starting materials readily available. The procedures are simple, and the conditions mild and readily amenable to large scale industrial synthesis. The method will, therefore, have wide application, and should open up the scope of triazine chemistry and further the application of triazines in chemical industry.

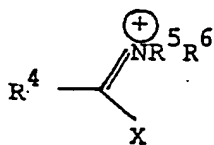
According to the present invention, there is provided a process for the synthesis of substituted 1,3,5-triazine compounds of the general formula I:



I

wherein R<sup>1</sup> and R<sup>2</sup>, which may be the same or different, are selected from the group consisting of hydrogen, halogen, alkoxy carbonyl, alkyl, substituted alkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkylamino, dialkylamino, arylamino, alkyl-aryl amino, alkylthio, arylthio, alkoxy and aryloxy (provided that R<sup>1</sup> and R<sup>2</sup> are not both halogen); and R<sup>3</sup> is selected from the group consisting of halogen, alkylamino, dialkylamino, arylamino, alkyl-aryl amino and N-heteroaryl;

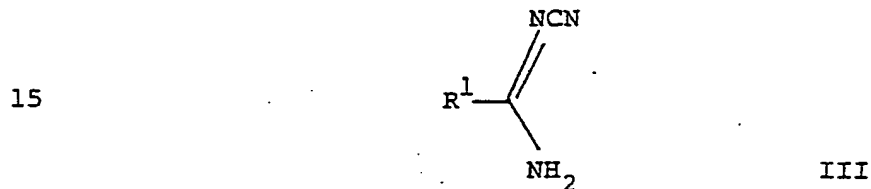
which comprises reaction of a halomethyleneiminium salt of the general formula II:



II



wherein  $R^4$  is selected from the group consisting of hydrogen, halogen, alkoxycarbonyl, alkyl, substituted alkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkylthio, arylthio, alkoxy and aryloxy;  
5  $R^5$  and  $R^6$ , which may be the same or different, are selected from the group consisting of hydrogen, alkyl and aryl (provided that  $R^5$  and  $R^6$  are not both hydrogen), or  $R^5$  and  $R^6$  together with the nitrogen atom to which they are attached form a saturated heterocyclic ring; X is  
10 halogen; and Y is an anion;  
with a compound of the general formula III:



wherein  $R^1$  is as defined above.

20 Compounds of the general formula III in which  $R^1$  represents hydrogen, halogen, alkoxycarbonyl, alkyl, substituted alkyl, aryl, substituted aryl, heteroaryl, or substituted heteroaryl are N-cyanoamidines. Where  $R^1$  represents alkylamino, dialkylamino, arylamino or  
25 alkyl-aryl-amino, the compounds III are N-cyanoguanidines. Similarly, where  $R^1$  represents alkoxy or aryloxy, the compounds III are N-cyanocarbamimidates; and where  $R^1$  represents alkylthio or arylthio, the compounds III are N-cyanocarbamidothioates.

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In the above general formulae, the alkyl groups preferably have 1 to 15 carbon atoms (including cycloalkyl groups of 4 to 8 carbon atoms), and suitable aryl groups include phenyl and naphthyl.

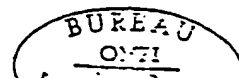
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Suitable heteroaryl groups include 5 or 6 membered heterocyclic groups having one or more hetero atoms (nitrogen, sulphur or oxygen) and include for example, indolyl and pyrazolyl groups. The substituents which may be present on the alkyl, aryl or heteroaryl groups include one or more substituents selected from the group consisting of halo (particularly chloro or bromo), alkyl (particularly lower alkyl having from 1 to 6 carbon atoms), alkoxy (particularly lower alkoxy having from 1 to 6 carbon atoms), alkylthio (particularly lower alkylthio having from 1 to 6 carbon atoms), aryl (particularly phenyl), aryloxy (particularly phenoxy), arylthio (particularly phenylthio), cyano, nitro, alkoxycarbonyl (particularly lower alkoxycarbonyl), amino and dialkyl-amino (particularly di (lower alkyl) amino). Halogen groups in the general formulae include bromo and, more preferably, chloro, whilst the anion represented by Y may be a bromide or chloride ion or an inorganic anion such as  $\text{OPOCl}_2^-$ .

25

The preferred procedure for the synthesis of this invention is to bring together the compounds of formula II and formula III in a suitable inert organic solvent. The following solvents have been found to be suitable: benzene, chloroform, methylene chloride, acetonitrile; the preferred solvent in most reactions being acetonitrile. Alternatively, phosphorus oxychloride may be used in excess as an inorganic solvent.

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The reaction mixture is then maintained at a suitable temperature (preferably between 0°C and 100°C) for an appropriate length of time (for example, from 15 min. to 6 days), then the 1,3,5-triazine is isolated by precipitation with water or extraction into an organic solvent after addition of water to the reaction mixture. In some cases neutralisation with sodium hydroxide solution is desirable to liberate all the triazine products from their salts. In cases when a mixture of triazines results, separation and purification of the components of the mixture can be effected by chromatography.

As an illustrative example of the process of the present invention, reaction of the chloromethyleneiminium salt (N,N-dimethylbenzamide-POCl<sub>3</sub> complex) with N-cyanobenzamidine in acetonitrile at room temperature gives 2-chloro-4, 6-diphenyl-1,3,5-triazine in 70% yield. Extension of the reaction to other chloromethyleneiminium salts, conveniently prepared in situ from N-substituted amides and POCl<sub>3</sub> or PCl<sub>5</sub>, gives the appropriately substituted 1,3,5-triazine in good yield. Other N-cyanoamidines react analogously, and examples of triazines so prepared are given in Table 1. It is found that in addition to chlorotriazines, small quantities of aminotriazines are sometimes formed, and that these become major products when N-arylamides are used as starting material (see Table 1). These aminotriazines may be formed in a secondary reaction between initially formed chlorotriazines and amines liberated during the cyclisation.



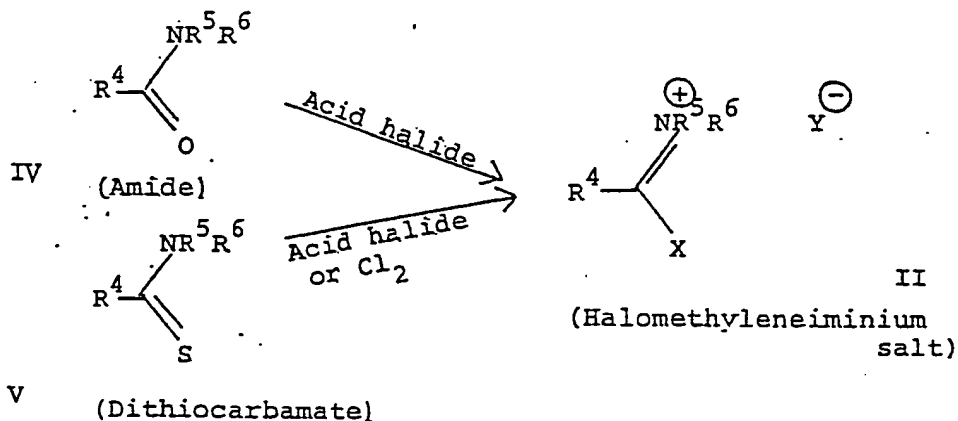


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The choice of conditions for the triazine synthesis is governed principally by the reactivity of the amide precursor of the chloromethyleneiminium salt: reactive amides such as dimethylformamide and dimethyl-  
 5 acetamide can be reacted with  $\text{POCl}_3$  in acetonitrile or other inert solvent at room temperature or below whereas unreactive amides such as benzanilide require  $\text{PCl}_5$  as the acid chloride component. As previously described in many cases  $\text{POCl}_3$  can be used in excess as solvent for the  
 10 reaction.

The N-cyanoamidines used in this synthesis are available by known methods from nitrile precursors via amidine or iminoether intermediates (Huffman and Schaefer, *supra*, Shaw and Adams, *supra*). The N-cyanoguanidines, N-cyanocarbamimidates and  
 15 N-cyanocarbamidithioates may be prepared by known methods also (E.Grigat and R.Pütter, *post.*; E.Allenstein, and R.Fuchs, Chem.Ber., 100, 2604 (1967); D.W.Kaiser, and D.Holm-Hansen, U.S.Patent 2697727).

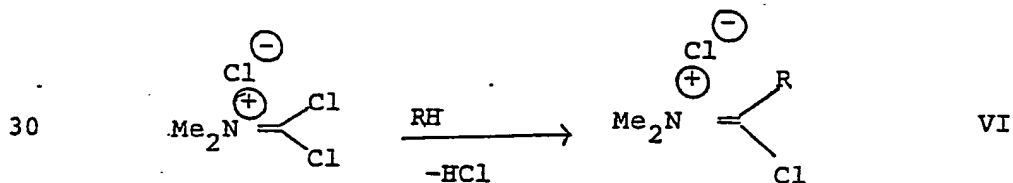
The halomethyleneiminium salts may be prepared  
 20 by known methods from amide and dithiocarbamate precursors - for a discussion on their preparation, see "Advances in Organic Chemistry", Vol.9, parts 1 and 2 (H. Bohme and H.G. Viehe, editors), "Interscience" (John Wiley and Co., N.Y.), 1976-1979. These methods may be illustrated  
 25 schematically as follows:



It has been found advantageous to prepare many of the halomethyleneiminium salts in situ from the appropriate amide precursor by reaction with an acid halide such as  $\text{POCl}_3$ ,  $\text{PCl}_5$  or  $\text{COCl}_2$  in a suitable solvent prior to the addition of the compound of the general formula III. When phosphorus oxychloride is used as the acid halide component it may sometimes be used in excess as solvent for the reaction.

Alkylthiochloromethyleneiminium salts (II,  $\text{R}^4 = \text{alkylthio}$ ) may also be prepared in situ from the appropriate dithiocarbamate and phosgene (Eilingsfeld and Mobius, Chem. Ber., 98, 1293, (1965)) and subsequently reacted with a compound of the general formula III in acetonitrile or phosphorus oxychloride as solvent.

Dichloromethyleneiminium salts may be generated from S,N,N-trialkyldithiocarbamates by reaction with chlorine. It is known that dichloromethyleneiminium salts may be reacted with activated aromatic or heterocyclic compounds, phenols or thiophenols to produce other reactive methyleneiminium salts in which one of the chlorines is displaced by an aryl, heteroaryl, aryloxy or arylthio group. This is shown schematically below, using dichloromethylenedimethyliminium chloride as example:



(see "Advances in Organic Chemistry" Vol.9 Parts 1 and 2, supra).



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The derived reagents VI are of course chloromethyleneiminium salts of the class II described earlier and may be generated in situ and used in the new triazine synthesis as described above. By way of example,

5 reaction of dichloromethylenedimethyliminium chloride with one equivalent of N,N-dimethylaniline for 15 min. in acetonitrile at reflux generates reagent VI where R = p-dimethylaminophenyl. Addition of N-cyanobenzamidine and further reflux gives, after work-up, 2-(p-dimethyl-

10 aminophenyl)-4-phenyl-6-chloro-1,3,5-triazine. Similarly, reaction of dichloromethylenedimethyliminium chloride with one equivalent of phenol in methylene chloride generates reagent VI where R = phenoxy, and further reaction with cyanobenzamidine gives 2-chloro-4-

15 phenoxy-6-phenyl-1,3,5-triazine.

The reaction of the present invention therefore represents a facile route to diversely substituted 1,3,5-triazines, many of which are not otherwise readily

20 accessible. In addition, the novel synthesis enables access to certain compounds of the general formula I above which are themselves novel.

Table 1 hereinafter illustrates the preparation

25 of a number of different substituted 1,3,5-triazine compounds in accordance with this invention:

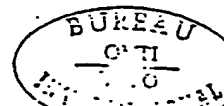


TABLE I

Chloromethylene- iminium salt R <sup>4</sup>	R <sup>5</sup> R <sup>6</sup> Y	N-cyano- amidine R <sup>1</sup>	Solvent/ Conditions	1,3,5-Triazine I R <sup>1</sup> R <sup>2</sup> R <sup>3</sup>	Yield (%)	m.p. (°C)	Molecular formula <sup>a</sup> or Lit.m.p.	Mass Spectrum <sup>b</sup>
Ph	Me Me OPOCl <sub>2</sub>	Ph	MeCN/4h reflux	a Ph Ph Cl	70	139	138-9	267
H	Me Me OPOCl <sub>2</sub>	Ph	MeCN/15 min. 25°	b Ph H Cl	56	86-87	C <sub>9</sub> H <sub>6</sub> ClN <sub>3</sub> (191.6)	191
Me	Me Me OPOCl <sub>2</sub>	Ph	C <sub>6</sub> H <sub>6</sub> /18h 25°	c Ph Me Cl	81	75	75.5-76.5	205
Me	H Ph OPOCl <sub>2</sub>	Ph	MeCN/1 h reflux	d Ph Me NMe <sub>2</sub>	5	63	C <sub>12</sub> H <sub>14</sub> N <sub>4</sub> (214.3)	214
Ph	H Ph Cl	Ph	MeCN/1 h reflux	e Ph Me NHPH	84	133	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> (262.3)	262
Indol-3-yl	Me Me OPOCl <sub>2</sub>	Ph	MeCN/6 days 25°	f Ph Ph NHPH	25	155	155	324
Cl	Me Me Cl	Ph	POCl <sub>3</sub> /15 min. reflux	g Ph Indol-3-yl Cl	47	195	C <sub>17</sub> H <sub>11</sub> ClN <sub>4</sub> (306.75)	306
MeS	Me Me Cl	Ph	POCl <sub>3</sub> /4 h reflux	h Ph Me <sub>2</sub> N Cl	85	105	C <sub>11</sub> H <sub>11</sub> ClN <sub>4</sub> (234.7)	234
Ph	Me Me OPOCl <sub>2</sub>	Me	MeCN/4h reflux	i Ph MeS Cl	56	89	C <sub>10</sub> H <sub>8</sub> ClN <sub>3</sub> (237.7)	237
				c Me Ph Cl	49	75		
				d Me Ph NMe <sub>2</sub>	5	63		

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TABLE 1 (cont'd)



Chloromethylene- iminium salt R <sup>4</sup>	R <sup>5</sup> R <sup>6</sup> Y	N-cyano- amidine R <sup>1</sup>	Solvent/ Conditions	1,3,5-Triazine I R <sup>1</sup> R <sup>2</sup> R <sup>3</sup>	Yield (%)	m.p. (°C)	Molecular formula <sup>a</sup> or Lit.m.p.	Mass Spectrum <sup>b</sup>
Ph	Me Me OPOCl <sub>2</sub>	ClCH <sub>2</sub>	MeCN/1 h reflux	j ClCH <sub>2</sub> Ph Cl	88	86-87	C <sub>10</sub> H <sub>7</sub> Cl <sub>2</sub> N <sub>2</sub> (240.1)	239
Ph <sub>2</sub> CH	-(CH <sub>2</sub> ) <sub>4</sub> - Cl	Ph	MeCN/48h reflux	k Ph Ph <sub>2</sub> CH N(CH <sub>2</sub> ) <sub>4</sub>	64	183-184	C <sub>26</sub> H <sub>24</sub> N <sub>4</sub> (392.48)	392
PhOCH <sub>2</sub>	Et Et OPOCl <sub>2</sub>	Ph	MeCN/4h reflux	l Ph PhOCH <sub>2</sub> Cl	67	81	C <sub>16</sub> H <sub>12</sub> ClN <sub>3</sub> O (297.74)	297
oToluy1	Me Me OPOCl <sub>2</sub>	Ph	POCl <sub>3</sub> /1h reflux	m Ph oToluy1 Cl	80	72-7	C <sub>16</sub> H <sub>12</sub> N <sub>3</sub> Cl (281.74)	281
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub>	H cyclo-OPOCl <sub>2</sub> Ph hexyl	Ph	MeCN/4h reflux	n Ph CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> Cl	87	44-5	C <sub>20</sub> H <sub>28</sub> ClN <sub>3</sub> (345.5)	345
PhCH <sub>2</sub>	Me Me OPOCl <sub>2</sub>	Ph	MeCN/4h reflux	o Ph PhCH <sub>2</sub> Cl	14	oil	C <sub>16</sub> H <sub>12</sub> ClN <sub>3</sub> (281.74)	281
H	Me Ph OPOCl <sub>2</sub>	Ph	MeCN/4h reflux	p Ph H N(Me)Ph	67	80	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> (262.30)	262
Me <sub>2</sub> N- 	Me Me Cl	Ph	MeCN/14h reflux	q Ph Me <sub>2</sub> N-  Cl	35		C <sub>17</sub> H <sub>15</sub> ClN <sub>4</sub> (310.5)	310
EtCOOCH <sub>2</sub>	H cyclo-OPOCl <sub>2</sub> Ph hexyl	Ph	MeCN/1h reflux	r Ph EtCOOCH <sub>2</sub> Cl	60		C <sub>13</sub> H <sub>12</sub> ClN <sub>3</sub> O <sub>2</sub> (277.5)	277

TABLE 1 (cont'd)

Chloromethylene- iminium salt R <sup>4</sup>	R <sup>5</sup> R <sup>6</sup> Y	N-cyano- amidine R <sup>1</sup>	Solvent/ Conditions	1,3,5-Triazine I R <sup>1</sup> R <sup>2</sup> R <sup>3</sup>	Yield (%)	m.p. (°C)	Molecular formula <sup>a</sup> or Lit.m.p.	Mass Spectrum <sup>b</sup>
PhO	Me Me Cl	Ph	CH <sub>2</sub> Cl <sub>2</sub> /2h reflux	s Ph PhO .Cl	53	103	C <sub>15</sub> H <sub>10</sub> ClN <sub>3</sub> O (283.71)	283
Ph	Me Me OPOCl <sub>2</sub>	PhO	MeCN/1h reflux	s PhO Ph .Cl	71	103	C <sub>15</sub> H <sub>10</sub> ClN <sub>3</sub> O (283.71)	283
	-(CH <sub>2</sub> ) <sub>4</sub> - OPOCl <sub>2</sub>	MeS	MeCN/1h reflux	t MeS  .Cl	62	92-3	C <sub>8</sub> H <sub>6</sub> ClN <sub>3</sub> OS (227.61)	227
pMeC <sub>6</sub> H <sub>4</sub>	Me Me OPOCl <sub>2</sub>	EtO	MeCN/1h reflux	u EtO pMeC <sub>6</sub> H <sub>4</sub> .Cl	80	78	C <sub>12</sub> H <sub>12</sub> ClN <sub>3</sub> O (249.70)	249
Ph	Me Me OPOCl <sub>2</sub>	Cl	CH <sub>2</sub> Cl <sub>2</sub> /18h Rm. Temp.	v Cl Ph .Cl	58	118-9	119-120	
Ph	Me Me Br	Ph	CH <sub>2</sub> Cl <sub>2</sub> /18h Rm. Temp.	w Ph Ph .Br	58	115	C <sub>15</sub> H <sub>10</sub> BrN <sub>3</sub> (312.17)	311
Ph	Me Me Cl	COOEt	CH <sub>2</sub> Cl <sub>2</sub> /18h Rm. Temp.	x COOEt Ph .Cl	41	70-71	C <sub>12</sub> H <sub>19</sub> ClN <sub>3</sub> O <sub>2</sub> (263.5)	263

- a. Microanalyses were in satisfactory agreement with calculated values (maximum deviation C  $\pm$  0.42, H  $\pm$  0.27, N  $\pm$  0.32).
- b. Mass spectra recorded on A.E.I. MS-9 instrument; molecular ions containing <sup>35</sup>Cl or <sup>79</sup>Br are shown.
- c. Or related compounds. See supra.

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1,3,5-triazines which can be prepared in accordance with the present invention have been found to exhibit fungal germination inhibition properties as shown in Table 2.

5

TABLE 2

Inhibition of Germination of Tilletia Foetida by  
1,3,5-Triazines

10

<u>1,3,5-Triazines</u>	<u>Spore Germination inhibition at 10 ppm (%)</u>
2-chloro-4-phenyl	100
2-chloro-4-phenoxyethyl-6-phenyl	100
15 2-N-methylphenylamino-4-phenyl	100
2-chloro-4-cyanomethyl-6-phenyl	100

20

The process of the present invention is further illustrated by the following specific examples:

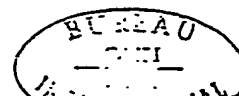
EXAMPLE 1

2-Chloro-4, 6-diphenyl-1,3,5-triazine (Ia):

25

N,N-Dimethylbenzamide (1.49 g, 10 mmol), is heated with POCl<sub>3</sub> (1 ml) on a steam bath at 100° for 5 min. The resulting complex is dissolved in acetonitrile (10 ml) and a solution of N-cyanobenzamidine (1.45 g, 10 mmol) in acetonitrile (20 ml) is added. After several minutes the triazine begins to separate; after 30 min water is added to complete the precipitation and the product is collected, washed with water and recrystallized from ethanol-water; yield: 1.8 g (70%); m.p. 139° (lit., 138-9°).

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EXAMPLE 22-Anilino-4-methyl-6-phenyl-1,3,5-triazine (Ie):

N-Cyanobenzamidine (1.45 g, 10 mmol),  
5 acetanilide (1.35 g, 10 mmol) and  $\text{POCl}_3$  (1 ml) are  
refluxed in acetonitrile (20 ml) for 1 h. The hydro-  
chloride of (Ie) precipitates as a pale yellow crystalline  
solid, m.p. 198-204°, and is collected after the mixture  
10 has been allowed to stand at room temperature over night  
(yield 2.5 g, 84%). The free triazine is obtained as  
colorless flat needles, m.p. 133° and is identical (m.p.,  
mixed m.p., nmr, ir and mass spectrum) with samples  
prepared by reaction of (Ic) with aniline in acetonitrile  
(reflux, 30 min) and from the reaction of N-phenyl-  
15 benzimidoyl chloride and N-cyanoacetamidine according to  
Ried and Kothe (Chem. Ber., 109, 2706, (1976).) The  
benzene-soluble fraction from the reaction mixture is  
washed with dilute ammonia, dried ( $\text{MgSO}_4$ ) and chromato-  
graphed on silica gel (Merck 70-30 mesh ASTM) eluting with  
20 benzene. The first fractions from the column contain (Ic)  
(0.075 g, 3.7%), m.p. 75° (lit. 75.5-76.5°).

EXAMPLE 32-Chloro-4-phenyl-6-methylthio-1,3,5-triazine (Ii):

25 S,N,N-Trimethyldithiocarbamate (1.35 g, 10 mmol)  
is dissolved in toluene (10 ml) containing phosgene (20%,  
w/v) and the solution kept at room temperature protected  
from moisture for 1 hr. The solvent and excess phosgene  
30 are evaporated in vacuo and to the residue is added  $\text{POCl}_3$   
(10 ml) and N-cyanobenzamidine (1.45 g). The mixture is  
refluxed for 30 min and poured into water. The product  
is extracted into benzene and purified by chromatography  
on silica gel eluting with benzene; the first fractions  
35 contain the methylthiotriazine (Ii) (1.3 g, 56%), m.p. 89°.





EXAMPLE 4

2-chloro-4-phenyl-6-(p-dimethylaminophenyl)-1,3,5-triazine  
(Iq):

5                   Dichloromethylene dimethyliminium chloride (1.9g)  
was suspended in acetonitrile (20 ml) and N,N-dimethyl-  
aniline (1.3 ml) added. The mixture was refluxed until all  
solids had dissolved (15 min.) then N-cyanobenzamidine  
10                   (1.45g) added. The mixture was refluxed a further 1½h and  
poured into water. An orange solid precipitated and after  
adjusting the pH to 5 with solid sodium acetate the  
mixture was allowed to stand at room temperature overnight.  
The solid was collected and recrystallised from ethanol to  
15                   give the dimethylaminophenyltriazine (1.1g 35%) as orange  
needles, m.p. 169-70°.

EXAMPLE 5

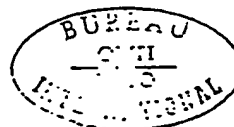
2-chloro-4-phenyl-6-undecyl-1,3,5-triazine (In):

20                   N-cyclohexyl dodecanamide (1.4g), phosphorous  
oxychloride (0.5 ml) and N-cyanobenzamidine (0.80g) were  
heated under reflux in acetonitrile (20 ml) for ½h. The  
mixture was poured into water and the solid collected.  
The product was purified by passage of its solution in  
25                   methylene chloride through a short column of silica gel;  
removal of the solvent from the eluate gave a pale tan  
oil which crystallised. Yield 1.5 g 87%, m.p. 44-45°.

30                   EXAMPLE 6

2-chloro-4-phenoxy -6- phenyl-1,3,5-triazine (Is):

METHOD A: Dichloromethylenedimethyliminium chloride (1.8g).  
was added to a stirred solution of phenol (1g) in dry  
35                   dichloromethane (50 ml). After 15 min a clear solution  
had resulted, to which was added N-cyanobenzamidine (1.45g).



The mixture was heated under reflux protected from moisture for 2 h, the solvent evaporated and the residue recrystallised from aqueous ethanol giving the phenoxy-triazine (Is) as colorless plates (1.8g, 53%), m.p. 103°.

5

METHOD B: Phosphorous oxychloride (0.4 ml) was added to N,N-dimethylbenzamide (0.6 g) dissolved in acetonitrile (10 ml). After 15 min at room temperature, N-cyano-O-phenylcarbamimidate (E.Grigat and R.Putter Chem. Ber., 98, 2619, (1965)) (0.65 g) was added and the mixture heated under reflux protected from moisture for 1 h. Water (100 ml) was added and the precipitate collected after 1 h and recrystallised from aqueous ethanol. The phenoxy-triazine (0.8 g, 71%) had m.p. 103° and was identical (nmr, mass spec, mixed m.p.) to that obtained by method A.

15

#### EXAMPLE 7

2-chloro-4(2<sup>1</sup>-furyl)-6-methylthio-1,3,5-triazine (It):

20

Phosphorous oxychloride (1 ml) was added to a solution of 2-furfuroylpyrrolidine (1.65 g) in acetonitrile (20 ml). After 15 min N-cyano-S-methylcarbamimidothioate (R.W.Turner, Synthesis, (1975), 332) (1.2 g) was added and the mixture heated under reflux protected from moisture for 1 h and then poured into water (100 ml). The precipitate was collected after 1 h and recrystallised from petroleum ether (bp 60-80°) to give the methylthiotriazine (It) as colorless needles (1.4 g, 62%), m.p. 92-93°.

25

30



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EXAMPLE 82-chloro-4-ethoxy-6-p-tolyl-1,3,5-triazine (Iu):

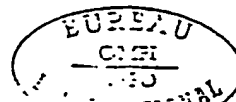
5 N,N-dimethyl-p-toluidamide (1.65 g) and phosphorous  
oxychloride (1 ml) were dissolved in acetonitrile (20 ml).  
To the solution was added N-cyano-O-ethyl carbamimidate  
(1.13 g) and the mixture heated under reflux protected  
from moisture for  $\frac{1}{2}$  h. Water (100 ml) was added and the  
precipitated product collected after 1 h at 0°C and  
10 recrystallised from aqueous ethanol to give the ethoxy-  
triazine (Iu) as colorless needles (2 g, 80%), m.p. 78°.

EXAMPLE 92,4-Dichloro-6-phenyl-1,3,5-triazine (Iv):

15 N,N-Dimethylbenzamide (1.5 g) and phosphorous  
oxychloride (1 ml) were dissolved in methylene chloride  
(20 ml) and the mixture kept at room temperature for 15  
min. N-Cyanochloroformamidine (1.1 g) (E. Allenstein,  
20 Z. Anorg. Allgem. Chem., 322, 265 (1963)) was added and  
the mixture stirred at room temperature overnight  
protected from moisture. The mixture was shaken with  
water (100 ml) and the organic phase separated, dried,  
concentrated in vacuo and applied to a column of silica  
25 gel (2 x 15 cm). Elution with benzene gave the dichloro-  
triazine (1.3 g, 58%) which crystallised from ethanol as  
colorless needles, m.p. 118-119° (lit 120°).

EXAMPLE 102-Bromo-4,6-diphenyl-1,3,5-triazine (Iw):

30 N,N-Dimethylbenzamide (1.5 g) was added to a  
stirred solution of phosphorous tribromide (2 ml) and  
bromine (1 ml) in methylene chloride (50 ml) and the  
35 mixture stirred protected from moisture at room temperature  
for 1 h. Cyclohexene (2 ml) was added to discharge the



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bromine colour, followed by N-cyanobenzamidine (1.45 g). The mixture was protected from moisture and stirred overnight. Water (100 ml) was added and stirring continued for 5 min. The organic layer was separated, dried and the solvent removed in vacuo. The product was purified by passage of its solution in methylene chloride through a short column of silica gel. Evaporation of the eluate and recrystallisation of the residue from ethanol gave the bromotriazine (Iw) as colorless fine needles (1.75 g, 58%), m.p. 155°.

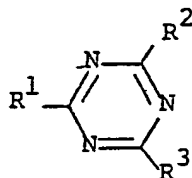
It will be appreciated by those skilled in the art that modifications and variations may be made to the specific details included herein without departing from the broad teaching of the present invention and the invention thus encompasses all such modifications and variations.



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## CLAIMS:

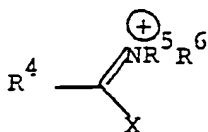
1. A process for the synthesis of substituted 1,3,5-triazine compounds of the general formula I:



I

wherein  $R^1$  and  $R^2$ , which may be the same or different, are selected from the group consisting of hydrogen, halogen, alkoxycarbonyl, alkyl, substituted alkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkylamino, dialkylamino, arylamino, alkyl-aryl amino, alkylthio, arylthio, alkoxy and aryloxy (provided that  $R^1$  and  $R^2$  are not both halogen); and  $R^3$  is selected from the group consisting of halogen, alkylamino, dialkylamino, arylamino, alkyl-aryl amino and N-heteroaryl;

which comprises reaction of a halomethyleneiminium salt of the general formula II:

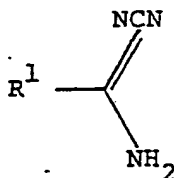


II

wherein  $R^4$  is selected from the group consisting of hydrogen, halogen, alkoxycarbonyl, alkyl, substituted alkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkylthio, arylthio, alkoxy and aryloxy;  $R^5$  and  $R^6$ , which may be the same or different, are selected from the group consisting of hydrogen, alkyl and aryl (provided that  $R^5$  and  $R^6$  are not both hydrogen), or  $R^5$  and  $R^6$  together with the nitrogen atom to which they are attached form a saturated heterocyclic ring; X is halogen; and Y is an anion;

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with a compound of the general formula III:



III

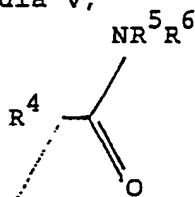
wherein R<sup>1</sup> is as defined above.

2. A process according to claim 1, wherein said reaction is carried out in an inert organic solvent.
3. A process according to claim 2, wherein said inert organic solvent is selected from the group consisting of acetonitrile, benzene, chloroform and methylene chloride.
4. A process according to claim 1, wherein said reaction is carried out in an excess of phosphorus oxychloride as an inorganic solvent.
5. A process according to any one of claims 1 to 4, wherein said substituted 1,3,5-triazine compounds are isolated from the reaction mixture by precipitation with water or by extraction into an organic solvent after addition of water.
6. A process according to claim 5, wherein said reaction mixture is neutralised prior to extraction of said substituted 1,3,5-triazine compounds.

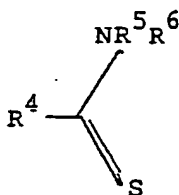


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7. A process according to any one of claims 1 to 6, wherein said halomethyleneiminium salt of the general formula II is prepared by reaction of an amide of the general formula IV; or a dithiocarbamate of the general formula V;



IV



V

wherein  $R^4$ ,  $R^5$  and  $R^6$  are as defined in claim 1, with an acid halide.

8. A process according to claim 7, wherein said acid halide is selected from  $\text{POCl}_3$ ,  $\text{POCl}_5$  or  $\text{COCl}_2$ .

9. A process according to claim 8, wherein said halomethyleneiminium salt is prepared in situ by reaction of an amide of the general formula IV as defined in claim 1 with phosphorus oxychloride, said phosphorus oxychloride being used in excess as solvent for the reaction.

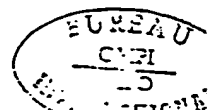
10. A process according to claim 1, substantially as herein described with reference to Table 1 or in any one of Examples 1 to 10.

11. Substituted 1,3,5-triazine compounds of the general formula I as defined in claim 1, whenever prepared by a process according to any one of claims 1 to 10.



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12. A substituted 1,3,5-triazine compound selected from the group consisting of 2-chloro-4-phenyl-1,3,5-triazine, 2-chloro-4-phenoxyethyl-6-phenyl-1,3,5-triazine, 2-N-methylphenylamino-4-phenyl-1,3,5-triazine and 2-chloro-4-cyanomethyl-6-phenyl-1,3,5-triazine.

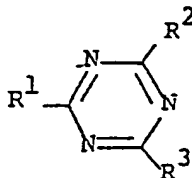




## AMENDED CLAIMS

(received by the International Bureau on 20 August 1981 (20.08.81))

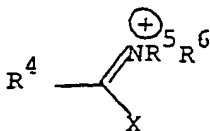
1. A process for the synthesis of substituted 1,3,5-triazine compounds of the general formula I:



I

wherein  $R^1$  and  $R^2$ , which may be the same or different, are selected from the group consisting of hydrogen, halogen, alkoxycarbonyl, alkyl, substituted alkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkylamino, dialkylamino, arylamino, alkyl-aryl amino, alkylthio, arylthio, alkoxy and aryloxy (provided that  $R^1$  and  $R^2$  are not both halogen); and  $R^3$  is selected from the group consisting of halogen, alkylamino, dialkylamino, arylamino, alkyl-aryl amino and N-heteroaryl;

which comprises reaction of a halomethylene-iminium salt of the general formula II:

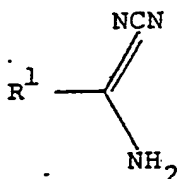


II

wherein  $R^4$  is selected from the group consisting of hydrogen, halogen, alkoxycarbonyl, alkyl, substituted alkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkylthio, arylthio, alkoxy and aryloxy;  $R^5$  and  $R^6$ , which may be the same or different, are selected from the group consisting of hydrogen, alkyl and aryl (provided that  $R^5$  and  $R^6$  are not both hydrogen), or  $R^5$  and  $R^6$  together with the nitrogen atom to which they are attached form a saturated heterocyclic ring; X is halogen; and Y is an anion;

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C 11

with a compound of the general formula III:



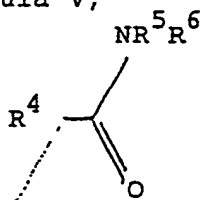
III

wherein  $R^1$  is as defined above.

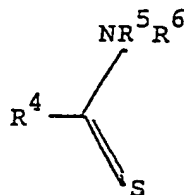
2. A process according to claim 1, wherein said reaction is carried out in an inert organic solvent.
3. A process according to claim 2, wherein said inert organic solvent is selected from the group consisting of acetonitrile, benzene, chloroform and methylene chloride.
4. A process according to claim 1, wherein said reaction is carried out in an excess of phosphorus oxychloride as an inorganic solvent.
5. A process according to any one of claims 1 to 4, wherein said substituted 1,3,5-triazine compounds are isolated from the reaction mixture by precipitation with water or by extraction into an organic solvent after addition of water.
6. A process according to claim 5, wherein said reaction mixture is neutralised prior to extraction of said substituted 1,3,5-triazine compounds.



7. A process according to any one of claims 1 to 6, wherein said halomethyleneiminium salt of the general formula II is prepared by reaction of an amide of the general formula IV; or a dithiocarbamate of the general formula V;



IV



V

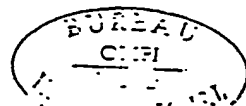
wherein  $R^4$ ,  $R^5$  and  $R^6$  are as defined in claim 1, with an acid halide.

8. A process according to claim 7, wherein said acid halide is selected from  $\text{POCl}_3$ ,  $\text{POCl}_5$  or  $\text{COCl}_2$ .

9. A process according to claim 8, wherein said halomethyleneiminium salt is prepared in situ by reaction of an amide of the general formula IV as defined in claim 7 with phosphorus oxychloride, said phosphorus oxychloride being used in excess as solvent for the reaction.

10. A process according to claim 1, substantially as herein described with reference to Table 1 or in any one of Examples 1 to 10.

11. Substituted 1,3,5-triazine compounds of the general formula I as defined in claim 1, whenever prepared by a process according to any one of claims 1 to 10.



## INTERNATIONAL SEARCH REPORT

International Application No

PCT/AU 81/00046

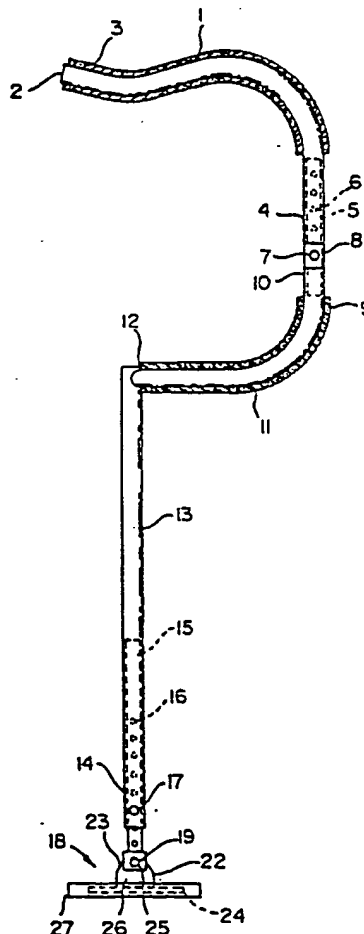
<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>3</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl. <sup>3</sup> C07D 251/16, 251/22, 405/04, 403/04		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>4</sup>		
Classification System	Classification Symbols	
IPC	C07D 251/16, 251/22, 405/04, 403/04	
US Cl.	544-187, -188, -189, -190, -194, -196, -197, -198, -199, -204, -205, -206, -207, -208, -209, -210, -211, -212, -213, -215, -216, -217, -218, -219.	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>4</sup>		
AU: IPC as above; Australian Classification 09.62-41		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup>		
Category <sup>5</sup>	Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
P,X	Australian Journal of Chemistry, Vol. 34, No. 3, issued 1981, March (CSIRO, Melbourne), R. Harris, "The Synthesis of Alkyl- and Aryl-Substituted 1,3,5-Triazines", see pages 623-34	1-12
X	Chemische Berichte, Vol. 109, issued 1976, Reid et al, "Über Umsetzungen von Chlorformamidinen und N-Phenyl-benzimidoylchlorid mit N-Cyanamidinen und 1-Cyanguanidin", see pages 2706 to 2715.	1
A	US, A, 3203550, published 1965, August 31, Schaefer.	1
A	US, A, 3154547, published 1964, October 27, Huffman	1
A	DE, A, 1178437, published 1964, September 24, Farbenfabriken Bayer AG.	1
A	Journal of Heterocyclic Chemistry, Vol. 7, issued 1970, August, Crenshaw et al. "A Synthesis of Isothiazoles and Pyrimidines via a Vilsmeier - Haack Reaction", see pages 871 to 873.	
<p><sup>14</sup> Special categories of cited documents: <sup>14</sup></p> <p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but on or after the priority date claimed</p> <p>"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search <sup>2</sup>	Date of Mailing of this International Search Report <sup>2</sup>	
29 June 1981 (29.06.81)	03 July 1981 (03-07-81)	
International Searching Authority <sup>1</sup>	Signature of Authorized Officer <sup>10</sup>	
AUSTRALIAN PATENT OFFICE	A.S. Moore. <i>AA Moore</i>	



US005318058A

**United States Patent** [19]  
**Zimmerman**[11] Patent Number: **5,318,058**  
[45] Date of Patent: **Jun. 7, 1994**[54] **SWING-FREE CRUTCH**[76] Inventor: **Dennis V. Zimmerman**, 909 North  
Villard, Tacoma, Pierce County,  
Wash. 98406[21] Appl. No.: **79,034**[22] Filed: **Jun. 21, 1993**[51] Int. Cl.<sup>5</sup> ..... **A61H 3/02**[52] U.S. Cl. .... **135/68; 135/71**[58] Field of Search ..... **135/68, 69, 71, 73,  
135/75, 77, 78, 79, 84; 248/188.8; 292/339, 338**[56] **References Cited****U.S. PATENT DOCUMENTS****3,738,674** 6/1973 Pauls ..... **135/71 X****FOREIGN PATENT DOCUMENTS****3004028** 8/1981 Fed. Rep. of Germany ..... **135/84***Primary Examiner*—Carl D. Friedman  
*Assistant Examiner*—Creighton Smith  
*Attorney, Agent, or Firm*—James F. Leggett[57] **ABSTRACT**

A novel improvement in a crutch device allowing for the rotational movement of the arms and elbows of the user while supporting his/her weight on a pair of these crutches, by displacing the vertical support means, between the under-arm rest and the hand rest, rearward a sufficient distance. This improvement, combined with an all terrain crutch pad and easy adjustable crutch length allows an individual with severe restriction in mobility from the waist down to play active sports, such as golf, and engage in employment requiring the free movement of hands and arms while maintaining mobility of the total person.

**1 Claim, 2 Drawing Sheets**

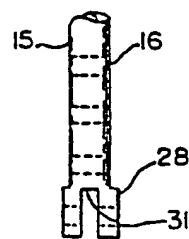
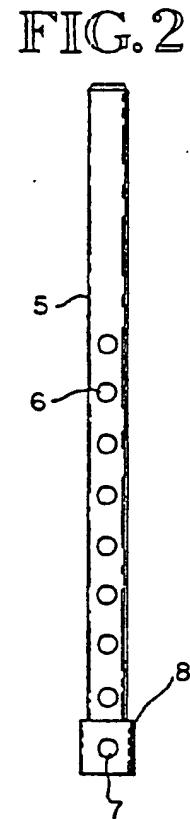
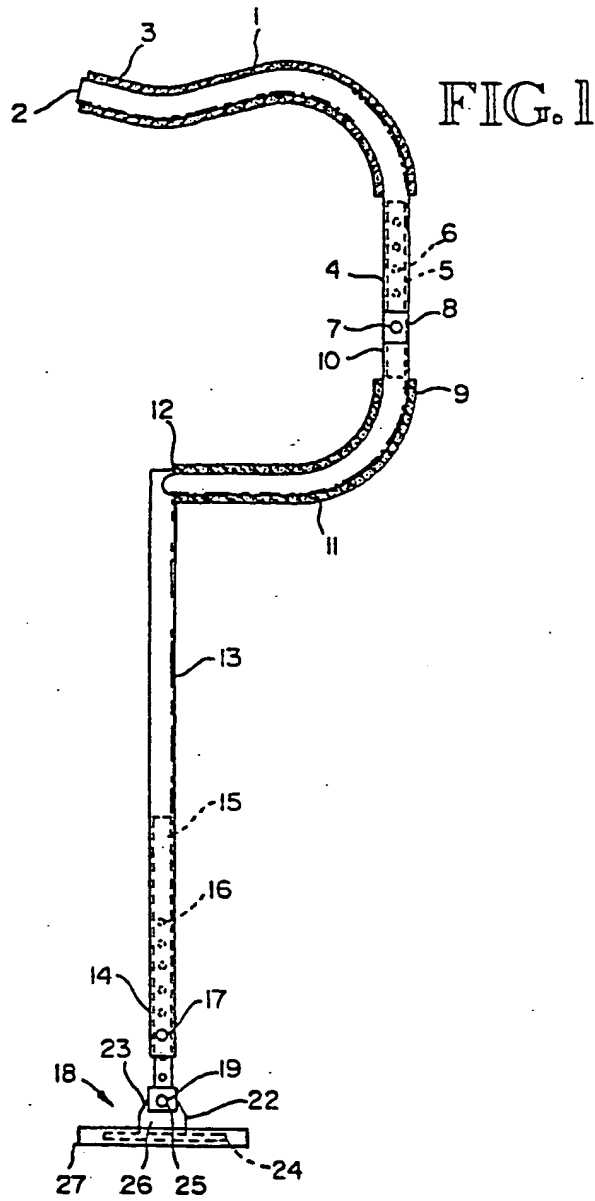


FIG. 4

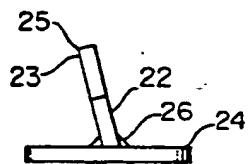


FIG. 5

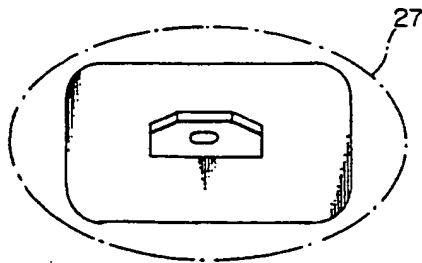
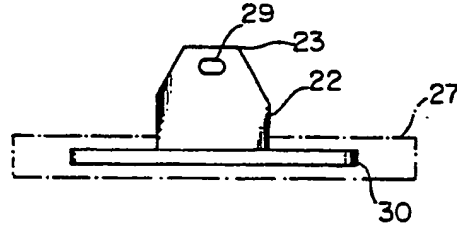


FIG. 6

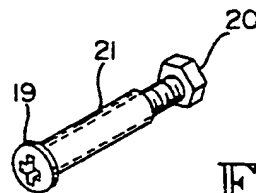


FIG. 7

## SWING-FREE CRUTCH

## BACKGROUND OF THE INVENTION

This invention relates generally to an improved vertical support means for individuals who have reduced control over their lower extremities, such as paraparetics, so that they may engage in physical activities which require free movement of their upper extremities, such as golf, while maintaining their mobility on uneven and unprepared terrain. More particularly, this invention involves displacing the vertical support between the underarm and the hand rest rearward a sufficient distance to allow the elbows of the user to swing in full travel while the weight of the user is suspended by the underarm portion.

In the past, light weight crutches, such as the Tubular Crutch disclosed in C. E. Murcott's U.S. Pat. No. 3,133,551, combined with expanded foot pads, such as those disclosed in K. A. Wilkinson's U.S. Pat. No. 4,899,771, have allowed more mobility on unprepared surfaces to individuals with limited use of their lower extremities. However, there has not been a device to allow such individuals to engage in active pursuits which require free rotation of the arms while in an upright position.

Therefore, the primary object of this invention is to provide people who have limited use of their lower extremities the opportunity to engage in physical activities, such as golf, which require free rotation of the arms while the torso remains upright. This invention will allow said individuals to engage in other work and recreational activities wherein upright mobility is required combined with the need to be able to freely swing their arms from the shoulder.

## SUMMARY OF THE INVENTION

The foregoing objectives are satisfied by this invention, which is comprised of a device having a reversely bent underarm portion running from in front of the underarm, in a semi-circular manner, so that it rises above the underarm at the rear and then extends rearward a sufficient distance, preferably 9 inches from front end to vertical, to accommodate the free swing of the elbows, and then makes a reverse bend to vertical. This vertical run of the invention is provided with an adjustment means to vary the height of the free swing area between the shoulder rest and the hand rest. The hand rest portion communicates with the adjustment means in a reverse bend from the vertical, to parallel the run of the underarm portion, extends a like distance and is provided with a semi-circular portion near its end to accommodate the user's hand. The underarm and the hand rest portions are comprised of suitable light weight material, such as tubular aluminum, and are covered with padding, such as foam rubber. The hand rest portion communicates fixedly with the vertical support which extends downward a sufficient distance, so that when the user is resting on the underarm portion the lower extremities are fully extended. This vertical support is also provided with a height adjustment means at its base, similar to that on the vertical section between the underarm and the hand rest, and is rotationally attached to an all terrain foot of suitable design.

The novel features of the invention will be best understood from the following description in light of the accompanying drawings. While particular embodiments of the present invention are shown and described,

it will be obvious to those skilled in the art that changes and modifications may be made without departing from this invention in its broader aspects and, therefore, the aim of the appended claims is to cover all such changes and modifications as fall within the true spirit and scope of this invention.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a side view of a crutch made according to my invention.

FIG. 2 is a side elevational view of the swing height adjustment means apart from the crutch.

FIG. 3 is a side elevational view of the height adjustment rod and its flange attachment fork apart from the crutch.

FIG. 4 is a front elevational view of the foot vertical support and inner foot apart from the crutch.

FIG. 5 is a side elevational view of the foot vertical support, inner foot and shoe print apart from the crutch.

FIG. 6 is a top elevational view of the inner foot and shoe print apart from the crutch.

FIG. 7 is an expanded view of the bolt or channel pin used to join the foot vertical support attachment flange to the height adjustment rod flange attachment fork.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

With reference to the drawings and particularly FIG. 1 thereof, the preferred embodiment of the Swing-Free crutch is shown.

The Swing-Free Crutch is comprised of a shoulder rest (1), a swing height adjustment means (4), an hand rest (11), a vertical support (13), a height adjustment means (14), and an all terrain foot (18). The shoulder rest (1), preferably consisting of  $\frac{1}{4}$  inch aluminum pipe (2), or other suitable light weight rigid material, being encased in foam padding (3), or other suitable cushioning material, having a reversely bent underarm portion running from in front of the underarm, in a semi-circular manner, so that it rises above the underarm at the rear and then extends rearward a sufficient distance, preferably 9 inches, to accommodate the free swing of the user's elbows and then makes a reverse bend to vertical, and adjustably communicates with the hand rest (11) by a swing height adjustment means (4).

As shown in FIG. 2, the swing height adjustment means (4) is comprised of a swing height adjustment rod (5), being of rigid construction and having an outside diameter slightly less than the inside diameter of the  $\frac{1}{4}$  inch aluminum pipe (2) of the shoulder rest, so that it slidably fits within the  $\frac{1}{4}$  inch aluminum pipe (2) and has adjustment holes (6) through its diameter regularly spaced at one inch intervals along its length, aligned so as to communicate with the 5/16ths diameter bolt with self locking nut (7) on the reinforcement collar (8) which is fixedly attached by usual means to the end of the shoulder rest (1), the end of the swing height adjustment rod (4) opposite to the end slidably inserted into the shoulder rest (1) through the reinforcement collar (8) being fixedly mounted to the inside of the contiguous end of the  $\frac{1}{4}$  inch aluminum pipe (10) of the hand rest (11). The vertical distance between the shoulder rest (1) and the hand rest (11) being variable by changing the point of engagement of the 5/16th diameter bolt with self-locking nut (7) in the adjustment holes (6) along the length of the swing height adjustment rod (5).



With further reference to FIG. 1, the hand rest (11), comprised of  $\frac{1}{2}$  inch aluminum pipe (10), or other suitable material, covered with foam padding (9), runs vertically from the swing height adjustment means (4) and reverse bends from the vertical to parallel the run of the shoulder rest (1) and extends a like distance and is provided with a semi-circular portion near its end to accommodate the user's hand. The hand rest (11) communicates fixedly by normal means, such as welding or bonding, with the vertical support (13), made of the same suitably rigid and hollow material as the shoulder rest (1) and the hand rest (11), such as  $\frac{1}{2}$  inch aluminum pipe, which extends downward a sufficient distance, so that the user, when resting on the underarm portion of the shoulder rest (1), has their lower extremities fully extended. This vertical support (13) is also provided with a height adjustment means (14) at its lower end which then rotatably attaches to an all terrain foot (18).

With reference to FIGS. 1, 3, 4, 5 & 6, the height adjustment means (14) is shown to be comprised of an height adjustment rod (15), of suitable rigid material and having an exterior diameter slightly smaller than the inside diameter of the vertical support (13), so that it can slide up and down within said vertical support (13), and provided with holes (16) regularly spaced along its length so as to communicate with a  $\frac{5}{16}$ th diameter spring pin (17) set into the base of the vertical support (13), so that the overall length of the vertical support (13) may be adjusted by engaging the  $\frac{5}{16}$ th diameter spring pin (17) in various of the holes (16). The bottom end of the height adjustment rod (15) expands in diameter to larger than the outside diameter of the vertical support (13) and forms an height adjustment rod flange attachment fork (28), which two tongs extend the length of the attachment flange (23) and are spaced sufficiently apart to accommodate the thickness of the attachment flange (23), and has a bolt or channel pin (19), equipped with a spacer collar (21) and retention nut (20), shown in FIG. 7, extending perpendicularly through the tongs of the height adjustment rod flange attachment fork (28) and through the hole in the attachment flange (29) of the all terrain foot (18) so that it is rotatable fore and aft in relation to the user of the Swing-Free Crutch, provided that the location of the hole in the attachment flange (29) is so located so that, when the bolt (19) is installed, the top face of the attachment flange (25) physically impinges on the crotch (31) of the height adjustment rod flange attachment fork (28) so that rotation of the attachment flange around the bolt (19) is limited from 0 to 15 degrees.

With specific reference to FIGS. 4, 5, & 6, the all terrain foot (18) is shown being comprised of a foot vertical support (22) and elliptical shaped inner foot (24), made of suitable flat rigid material such as aluminum, having an attachment flange (23) at its top of tapering width and provided with a hole in the attachment flange (29) to accommodate the bolt or channel pin (19), and being attached at the base of its foot vertical support (22) to an inner foot (24), of suitably rigid material, by standard weld means (26) and oriented at 15 degrees from perpendicular to the inner foot (24) toward the user, so that the swing-free crutch is comprised of a right and left. A removable shoe print (27), made of suitable material such as rubber or leather, is attached beneath the inner foot (24) by means of slots (30) molded into the top of the shoe print (27) being of sufficient dimension to removably accommodate the inner

foot (24) and having a suitable non-skid tread on its bottom face.

While particular embodiments of the present invention have been shown and described, it will be obvious to those skilled in the art that changes and modifications may be made without departing from this invention in its broader aspects and, therefore, the aim in the appended claims is to cover all such changes and modifications as fall within the true spirit and scope of this invention.

I claim:

1. A crutch wherein a vertical support between a shoulder rest and a hand rest is displaced rearward, being comprised of a shoulder rest means, a swing height adjustment means, a hand rest means, a vertical support means, a height adjustment means and an all terrain foot means wherein:

said shoulder rest means is comprised of rigid hollow pipe which extends in a semi-circular manner, extending rearward, then makes a reverse bend to vertical adjustably communicating with a swing height adjustment means;

said swing height adjustment means being comprised of a swing height adjustment rod of suitable rigid material having an outside diameter slightly less than an inside diameter of the rigid hollow pipe of the shoulder rest so that it slidably fits therein and having regularly spaced holes through it at one inch intervals along its length aligned so as to accommodate a bolt secured by a self locking nut which extends from a reinforcement collar of suitably rigid material which is fixedly attached to an end of the shoulder rest by standard weld or bonding means and an end of the swing height adjustment rod opposite to an end extending into the shoulder rest is rigidly fixed into an end of a hand rest means by standard weld or bonding means so that vertical distance between the shoulder rest and hand rest is adjustable by engaging the bolt in different holes along the length of the swing height adjustment rod;

said hand rest means is comprised of rigid hollow pipe which extends vertically from the swing height adjustment then makes a reverse bend to parallel the shoulder rest a like distance, having within and near its end a semi-circular portion, and is joined by standard weld or bonding means to a vertical support means at its top;

said vertical support means being comprised of rigid hollow pipe which extends vertically, and includes a height adjustment means at its lower end;

said height adjustment means being comprised of a height adjustment rod of suitable rigid material having an outside diameter slightly less than the inside diameter of the pipe of the vertical support so that it slidably fits therein and having regularly spaced holes through it at one inch intervals along its length aligned so as to accommodate a spring pin set by standard means near the lower end of the vertical support so that the vertical support may be adjusted and said height adjustment rod, at its lower end, expands in diameter to larger than the outside diameter of the vertical support and forms a height adjustment rod flange attachment fork having two tongs, extending downward a sufficient length and spaced sufficiently apart so as to accommodate an attachment flange of an all terrain foot means, and having a bolt or channel pin, equipped

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with a spacer collar, and held in place by a standard retention nut means, extending perpendicularly through the tongs of the height adjustment rod flange attachment fork and through a hole in an attachment flange of an all terrain foot means, said hole being located on an attachment flange so that, when the bolt is installed, a top face of the attachment flange physically impinges on a crotch of the height adjustment rod flange attachment fork so that rotation of the attachment flange around the bolt is limited from 0 to 15 degrees;

said all terrain foot means, being made of suitable flat rigid material, is comprised of a foot vertical support, extending from the top of an elliptically shaped inner foot vertically and having an attach-

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ment flange at its top end and being attached by standard weld means to the top of the inner foot at 15 degrees from perpendicular toward the user at a point so that the foot vertical support is positioned in a center of the elliptically shaped inner foot of the crutch, so that there is a right hand and a left hand crutch, and a shoe print means made of suitable material such as rubber or leather, being slightly larger in diameter than the elliptically shaped inner foot, equipped with slots molded into and around the top edge of the shoe print to removably accommodate the thickness of the elliptically shaped inner foot and having a suitable non-skid tread on its bottom face.

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